

# PATENT SPECIFICATION

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## (54) MODIFIED POLYMER COMPOSITION AND A PROCESS FOR PRODUCING THE SAME

(71) We, ASAHI KASEI KOGYO KABUSHIKI KAISHA a Japanese Company of 25-1, 1-chome, Dojima-Hamadori, Kita-ku, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to modified mono-olefin polymer compositions and to processes for producing the same.

More particularly, this invention provides a process for the production of a modified polymer composition having excellent mechanical properties essentially consisting of a mono-olefin polymer obtained by graft and/or block copolymerizing the mono-olefin polymer with a vinyl monomer, and a vinyl homopolymer.

Ever since the discovery made by Ziegler and Natta with regard to the stereospecific polymerization, the crystalline olefin polymers have been greatly developed on a commercial scale and they have established an important position as general purpose resins in the industry.

However, the crystalline olefin polymers *per se* have some disadvantages. For example, propylene polymer has a drawback in that, notwithstanding its excellent rigidity it may not be used successfully in fields where a high impact resistance is required, due to its unsatisfactory low temperature characteristics.

In order to overcome such fundamental drawbacks of crystalline olefin polymers, there have been proposed at first simple random copolymerization and blending of the olefin polymers with various elastomers and other polymers. However, the methods hitherto proposed are unsatisfactory since, for example, an attempt to improve, impact resistance of an olefin polymer to a practical extent according to such methods inevitably leads to deterioration in other properties such as hardness, modulus of elasticity and tensile strength.

Various ethylene-propylene block copolymers have been announced, e.g. under the trade names of "Polytelomer" (Product of Eastman Kodak Co.) and "Olemer" (Product of Avisun), which are stated to have improved and well-balanced properties.

Nevertheless, the degree of modification of olefin polymers achieved by the prior methods has been still insufficient and the problem of the development of a product having both excellent rigidity and impact resistance has remained unsolved.

In the past, the method of modifying olefin polymers by graft copolymerizing the same with other polymerisable monomers has been thoroughly studied and found to be very useful, and as a result, various processes for graft copolymerization have been proposed. However, very few of these processes have been satisfactory from a commercial standpoint; some of them involve quite complicated operations and others are incapable of allowing continuous operation on a commercial scale.

For example, although a process for graft copolymerization using radioactive irradiation is well known, the process requires special equipment and techniques and so may not be adopted readily and generally.

A process for graft copolymerization is known in which a polymer is dissolved or dispersed in a suitable solvent or polymerization medium and the resulting solution or dispersion is brought into contact with a vinyl monomer in the presence of a radical generating initiator such as a peroxide, or, alternatively, the polymer may be first reacted with the radical generating initiator and then contacted with the vinyl monomer. The process, however, requires a large amount of solvent or polymerization medium and involves quite complicated processing, and so is unsatisfactory from the economic and operation standpoints.

It has also been proposed to react a vinyl

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monomer with an olefin polymer at a temperature above the melting point of the olefin polymer using a radical generating initiator in the absence of solvent or polymerization medium. For example, Belgian Patent No. 569,958 discloses a process in which an olefin polymer is cross-linked with a vinyl monomer by heating them at a temperature of 120—200°C. in the presence of a free radical generator.

Furthermore, U.S. Patents No. 3,177,269 and No. 3,177,270 describe a process in which an olefin polymer is heated at 110—250°C. and, after being mixed with a specific vinyl monomer and an organic peroxide in order to prevent the decomposition and deterioration of the olefin polymer, the olefin polymer is reacted with the vinyl monomer. However, the process has a fundamental drawback in that the composition ratio of the remaining unreacted olefin polymer, the resulting modified copolymer and vinyl polymer in the resulting polymer composition with respect to a given vinyl monomer is invariably constant and the ratio cannot be changed optionally.

There is described in British Patent No. 963,771 a process in which an olefin polymer is mixed with a radical generating initiator, and a vinyl monomer is added to the resulting mixture to react therewith. However, similarly, the process is unsatisfactory from the commercial point of view in that the type of usable monomer is restricted since the reaction is carried out either in solid or liquid phase, and the radical efficiency is quite low.

It is, accordingly, an object of the invention to provide modified mono-olefin polymer compositions having improved mechanical properties.

We have conducted a thorough study with regard to the relationship between a composition of a modified polymer composition obtained by graft or block copolymerizing a mono-olefin polymer with a vinyl monomer copolymerizable therewith, and performance thereof. As a result, we have unexpectedly found that the presence of vinyl polymer which is not bound to mono-olefin polymer (hereinafter referred to simply as "vinyl homopolymer") in the modified polymer composition serves quite effectively for the modification of performance of the modified polymer composition under the co-existence of vinyl polymer which is graft or block copolymerized with the mono-olefin polymer (hereinafter referred to simply as "copolymerized vinyl polymer"). We have further found that the ratio of vinyl homopolymer to copolymerized vinyl polymer in the modified polymer has a very important influence on the mechanical properties of the modified polymer.

Thus the most desirable modification of the mono-olefin polymer can be accomplished by properly selecting the amounts and ratio of copolymerized vinyl polymer and vinyl homo-

polymer contained in the modified polymer composition.

According to the present invention, therefore, there is provided a process for the production of a modified mono-olefin polymer composition which comprises treating a mono-olefin polymer (as herein defined) with a radical-generating initiator and reacting the product with a vinyl monomer (as herein defined) in the molten state and with agitation of the reaction mixture, whereby part of the vinyl monomer is graft or block copolymerized with the mono-olefin polymer and part is polymerized *per se*, the total of the vinyl monomer thus copolymerized or polymerized constituting 3 to 30% by weight based on the weight of the mono-olefin polymer and the proportion of the said total of vinyl monomer so polymerized or copolymerized which is graft or block copolymerized with the mono-olefin polymer being 10 to 65% by weight of such total.

By the term "mono-olefin polymer" use herein is meant a homopolymer of a mono-olefin, which is an aliphatic or aromatic hydrocarbon which contains an ethylenically unsaturated group, a copolymer of a said mono-olefin with another mono-olefin or a copolymer of a said mono-olefin with another ethylenically unsaturated compound copolymerizable therewith.

By the term "vinyl monomer" is meant a compound containing a vinyl or vinylidene grouping. Since a plurality of such vinyl monomers may be employed in the process of the invention the vinyl polymer content of the final composition may be either a homopolymer of a single vinyl monomer or a copolymer of two or more such vinyl monomers.

Mono-olefin base polymers referred to herein include mono-olefin homopolymers such as low or high density polyethylene, polypropylene, polybutene-1, poly-3-methylbutene-1, poly-4-methylpentene-1 and polystyrene; copolymers of mono-olefins with other olefin or vinyl monomers such as ethylene/propylene copolymer, ethylene/propylene block copolymer, ethylene/butene copolymer, ethylene/vinyl acetate copolymer, ethylene/ethylacrylate copolymer, and propylene/4-methylpentene-1 copolymer; and mixtures thereof.

Vinyl monomers which may be used in this invention include:

(1) Styrene and styrene derivatives, for example, styrene,  $\alpha$ -methylstyrene and o-methylstyrene.

(2) Acrylic, methacrylic acids and esters, amides or metal salts thereof, for example, acrylic acid, methacrylate, butyl acrylate, lauryl acrylate, stearyl acrylate, acrylic amide, sodium acrylate, calcium acrylate, methacrylic acid, methyl methacrylate, butyl methacrylate, lauryl methacrylate, cyclohexyl methacry-

late, glycidyl methacrylate, methacrylate amide, sodium methacrylate and calcium methacrylate.

(3) Vinyl esters and allyl esters, for example, vinyl butyrate, vinyl laurate, vinyl stearate, vinyl adipate, allyl acetate and allyl laurate.

(4) Polycyclic and heterocyclic vinyl compounds, for example, vinyl naphthalene, N-vinylcarbazole, vinyl pyridine and vinyl pyrrolidone.

(5) Other monoethylenically unsaturated monomers, for example, acrylonitrile, methacrylonitrile and vinylketone, and

(6) Monomers having 2 or more vinyl groups, for example, divinylbenzene, ethylenedimethacrylate, diethylenedimethacrylate, polyethylenedimethacrylate, divinyladipate, diallyl-maleate, diallylphthalate, allyl acrylate, triallyl phosphite, diallylcyanurate and triallylcyanurate.

These monomers exemplified above may be used in admixtures of two or more kinds, and a mixture sometimes affords advantages when working on a commercial scale.

In other words, it is particularly desirable to use these vinyl monomers having different characteristics from each other in admixture of two or more kinds considering the polarity of substituent groups of these vinyl monomers or the glass transition temperature of the vinyl polymer, in order to improve the properties of both, such as printability and adhesiveness vs. electrostatic characteristics and surface abrasion, or modulus of elasticity, hardness and rigidity vs. impact strength and flexibility.

In the modified polymer composition produced by the process of this invention, the amount of vinyl polymer with respect to the mono-olefin base polymer, i.e. the sum of copolymerized vinyl polymer and vinyl homopolymer is 3—30% by weight based on the weight of mono-olefin base polymer. The amounts less than 3% by weight may not afford any practical modifying effect, while the amounts exceeding 30% by weight lead to a deterioration in the properties originally belonging to mono-olefin polymer.

As described hereinbefore, in the modified polymer composition, the ratio of copolymerized vinyl polymer to vinyl homopolymer is a very important factor for the modifying effect on the mechanical properties of mono-olefin polymers in which the object of this invention resides. Thus, if the ratio of copolymerized vinyl polymer to vinyl homopolymer is extremely large, or, only a completely copolymerized vinyl polymer is present in the modified polymer composition, then, the improving effect on the mechanical properties of mono-olefin base polymer may be unsatisfactorily small.

On the other hand, if the ratio of copolymerized vinyl polymer to vinyl homopolymer is extremely small, or, only vinyl homopoly-

mer is present, i.e. the resulting polymer composition is a simple blend consisting of mono-olefin base polymer and vinyl homopolymer, certain properties of the resulting modified polymer may be improved to some extent, but desirable properties originally belonging to mono-olefin polymer are greatly degraded.

Thus, a remarkable modifying effect may be obtained only when the ratio of copolymerized vinyl polymer to the sum of vinyl homopolymer and the copolymerized vinyl polymer is in a particular range, which is 10—65% by weight.

In the modified polymer composition prepared in this invention, although it is desirable that the mono-olefin base polymer is completely either graft or block copolymerized with vinyl polymer, this does not prevent the presence of non-bound mono-olefin polymer in the modified composition.

In preparing the modified polymer composition it is possible to obtain the same by subjecting a mixture of a mono-olefin polymer and a vinyl monomer to the action of a radical generating initiator such as peroxide to graft or block copolymerize the vinyl monomer therewith, and blending the resulting copolymer mechanically with a polymer of said vinyl monomer.

However, more preferably a modified polymer composition having particularly preferable performances may be obtained by producing a copolymer in which vinyl monomer is graft or block copolymerized with mono-olefin polymer, and vinyl homopolymer altogether in a single polymerization reaction while adjusting the ratio of copolymerized vinyl polymer to vinyl homopolymer within the range set forth herein, and this process can be practised easily on a commercial scale.

More practically, the process of this invention for producing the modified polymer composition may be suitably carried out by reacting mono-olefin polymer with a radical generating initiator selected from organic peroxides, inorganic peroxides, azo compounds or organotin compounds by heating them, and reacting the resulting molten polymer radical with vinyl monomer with agitation under such a condition that the polymer radical and unreacted radical generating initiator are present at a predetermined ratio.

The composition of the polymer composition obtained according to the process mentioned above may be altered by either suitably selecting the period during which after the mixture of mono-olefin polymer and radical generating initiator is reacted by heating, the resulting mixture is contacted with vinyl monomer, or, by selecting the type and amount of radical generating initiator having an optimum radical generating rate when the process is practised under a reaction conditions including predetermined temperature and

period. The above alternatives may be used in combination, if required.

Free-radical-generating initiators which may be used in the process of this invention are conventional compounds known well as radical polymerization initiators including, for example, dialkyl peroxides such as di-*t*-butyl peroxide, dicumyl peroxide,  $\alpha,\alpha'$ -bis(*t*-butyl-peroxy)-*p*-diisopropylbenzene, and 2,5-dimethyl-2,5-di(*t*-butyl-peroxy) hexane; hydroperoxides such as *t*-butylhydroperoxide, cumylhydroperoxide, and *p*-menthane hydroperoxide; diacyl, ester and ketone peroxides such as benzoyl-peroxide, lauroyl-peroxide, *t*-butyl peracetate, *t*-butylperbenzoate and cyclohexane peroxide. In addition to these exemplified above, azo compounds, azide compounds, inorganic peroxides or unstable halogenated hydrocarbons which are decomposed at above 100°C. may also be effectively used.

In practising the process of this invention, the conventional sealed-pressurized agitating vessel, kneader, Banbury mixer and screw extruder may be conveniently used. Although the reaction of this invention may be satisfactorily conducted in the presence of oxygen, it is more preferable to conduct the reaction in the absence of oxygen. Thus, the use of an equipment capable of conducting the reaction in a substantial absence of oxygen is desirable.

Since it is of extreme importance to carry out the reaction with sufficient mixing of reactants by agitation, the use of a screw extruder provided with mixing torpedos, or a Banbury mixer is recommended.

In practising the process of this invention, it is an essential requisite to conduct the reaction in a molten state and the reaction temperature is preferably within the range of from the melting point of mono-olefin polymer used to 100°C. above that point.

The reaction period is somewhat variable depending upon the reaction conditions employed. However, in general, the reaction can be completed in a very short period of time. e.g. 30 minutes.

The requirement for such a short reaction time in the process of this invention gives an advantage in practising the process on a commercial scale. Thus, the simplest and most advantageous way of practising the present process continuously on a commercial scale is to conduct the modification of polymers according to this invention and pelletizing of the modified polymers at the same time by using a screw extruder-type pelletizing machine.

Normally, in the production of resin materials, there is involved a pelletizing process in which the screw extruder-type pelletizing machine is conveniently used. In general, the heating time in such a pelletizing machine e.g. about 30 minutes conveniently corresponds

to the reaction time required in the process of this invention.

Thus, the mode of continuous working of the process of this invention using the screw extruder-type pelletizing machine will be explained hereinafter.

An olefin polymer, e.g. a crystalline propylene polymer, is mixed uniformly with a radical initiator, e.g. dicumyl peroxide, and the resulting mix is put into a hopper of a screw extruder provided with mixing torpedos.

Meanwhile, a vinyl monomer, e.g. lauryl methacrylate, is supplied quantitatively through a hole provided at a suitable position of the extruder so that the vinyl monomer may be mixed and kneaded uniformly with the molten monolefin polymer in which monolefin radical and unreacted radical generating initiator are present in a predetermined ratio. Then, the polymer mix is melt extruded while being reacted with agitation.

A modified polymer composition was prepared according to the procedures described above by graft/block copolymerizing lauryl acrylate with propylene polymer. In this polymer composition, the content of lauryl acrylate copolymerized with propylene polymer was 2.0%, the content of lauryl acrylate homopolymer was 2.7%, i.e. the total content of lauryl acrylate polymer was 4.7%, and the ratio of lauryl acrylate copolymerized with propylene polymer to the sum of lauryl acrylate homopolymer and lauryl acrylate copolymerized with propylene polymer was 43%.

The mechanical properties of the above-mentioned polymer composition were measured with the results that the drop-cone impact strength at -20°C. was 3.1 kg-m and the Rockwell hardness (R scale) was 78.

By comparing these values with those of unmodified, original propylene polymer, i.e. the impact strength of 0.09 kg-m and the Hardness of 82, it can be readily appreciated that the low temperature impact resistance, which is a big handicap in the performance of propylene polymer, is remarkably improved, while no important deterioration is effected on the hardness which is a desirable property of propylene polymer, thus, a well-balanced modification of the physical properties has been achieved.

In contrast, a simple blended propylene polymer containing 5% by weight of lauryl acrylate homopolymer has an impact strength of 1.8 kg-m and a hardness of 66. True as it is that the impact strength has been fairly improved, the hardness which is a feature of propylene polymer, has been drastically deteriorated, thus, it cannot be said that a desirable modification has been accomplished from the practical point of view.

On the other hand, a modified propylene polymer containing 5% of lauryl acrylate polymer graft/block copolymerized therewith has an impact strength of 0.48 and a hardness of

80, showing that the modifying effect on the impact strength is quite small.

Thus, it should be understood that a well-balanced modification of physical properties of mono-olefin polymer can be accomplished distinctively when the mono-olefin polymer contains a certain specific proportion of vinyl homopolymer in co-existence with vinyl polymer copolymerized with the mono-olefin base copolymer.

In the process for modifying mono-olefin polymers using the screw extruder-type pelletizing machine explained hereinabove, the period during which vinyl monomer is contacted and reacted with agitation may be adjusted by altering the extrusion rate and position of the hole through which vinyl monomer is supplied into the mix provided on the cylinder portion of the machine. The changing of the ratio of graft or block copolymer to vinyl homopolymer may also be accomplished by suitably choosing the reaction temperature, the type of radical generating initiator, the proportion of monomer to the radical generating initiator, etc., in addition to the adjustment of the contacting period of the monomer mentioned above.

By the combination of these adjusting means, it is possible to vary the ratio by weight of graft or block copolymer to vinyl homopolymer in a wide range, e.g. 2:1 to 1:20. Moreover, as a means for adjusting the content of mono-olefin base polymer, there may be used various conditions, including, for example, the alteration of the proportion of vinyl monomer to mono-olefin polymer.

The amounts of vinyl monomer and radical generating initiator vary in a wide range depending upon the kind and degree of modification contemplated and the reaction conditions. However, in general, the amount of vinyl monomer ranges from 0.1—50% by weight and that of radical generating initiator ranges from 0.01—5% by weight, both based on the weight of total polymer composition.

As can be noted from the foregoing description, in accordance with the present invention, there may be accomplished an excellent modification of the physical properties of mono-olefin polymers as compared with those of mono-olefin copolymers containing no vinyl homopolymer or a simple polymer blend obtained by blending mono-olefin polymers with vinyl homopolymer.

What is more surprising is a finding that the physical properties of the modified polymer composition produced in this invention by graft/block copolymerizing mono-olefin base polymer with vinyl monomer and simultaneously mixing the resulting graft/block copolymer intimately with vinyl homopolymer produced in the above-mentioned reaction are completely different from those of mono-olefin polymer compositions obtained by a polymerization reaction in which the forma-

tion of vinyl homopolymer is suppressed as low as possible, or, removing the vinyl homopolymer produced in the polymerization reaction by a solvent extraction and blending therewith a suitable amount of vinyl homopolymer obtained according to a conventional vinyl polymerization. For example, it has been found that the polymer composition of this invention has far superior mechanical properties such as impact strength over those conventional polymer compositions known heretofore.

It is a surprising and unexpected effect which characterizes this invention that there is a remarkable difference between the mechanical properties of the modified polymer composition and those of conventionally known polymer compositions in spite of the fact that both of them contain the same vinyl homopolymer as a common ingredient.

While the modified polymer composition produced by this invention has various excellent performances, the modifying effect on various mechanical properties, e.g. impact resistance, hardness, modulus of elasticity, tensile strength and creep characteristic is particularly remarkable and, in addition, the affinity with dyes and adhesiveness with metals are also enhanced.

These improvements and enhancements will become apparent in the Examples described hereinafter.

Whereas the modified polymer composition produced by this invention may be suitable for various uses, particularly, it may be successfully used in the field of manufacture of shaped articles, sheets and films.

In practising the process of this invention using ultra-high molecular weight  $\alpha$ -olefin polymers as olefin polymers, the working may be carried out in combination with a process for improving the processability of the  $\alpha$ -olefin polymers, by lowering the molecular weight thereof, which are otherwise very difficultly or impossibly melted due to their extremely high molecular weight, because the radical generating initiator enhances the breaking of molecular chain, of the polymers at high temperatures. In other words, the improvement of the processability of ultra-high molecular weight  $\alpha$ -olefin polymer and the modification according to this invention can be accomplished simultaneously.

The process of this invention may be practised in the presence of various additives such as pigments, inorganic materials, plasticizers, heat or light stabilizers, etc. However, more preferably, suitable types and amounts of additives are incorporated in the polymers after being modified according to the process of this invention depending upon the uses of the modified polymers contemplated.

This invention will be explained more fully and practically in the following Examples.

In the following Examples, percentages re-

ferred to therein are % by weight based on the weight of mono-olefin polymer, unless otherwise specifically indicated.

- 5 The values of drop-cone impact strength, Izod impact strength, hardness and tensile strength of the modified polymer compositions referred to therein were measured according to the following procedures.

- 10 Sample polymer compositions were shaped into test pieces by a compression-moulding machine. After these test pieces were conditioned for 72 hours, their physical properties were measured as follows:

Drop-cone impact strength at  $-20^{\circ}\text{C}$ :

- 15 A test piece of 2 m/m thickness cooled at  $-20^{\circ}\text{C}$ . for an hour was given an impact by dropping a weighted cone thereon from a predetermined height and the energy required to destroy the test piece in terms of kg-m was measured by using a Falling Missile Impact Test made by Toyo Seiki Mfg., Co.

Izod impact strength:

ASTM D256—56

Unit: Ft-lb/in (Notched)

- 25 Rockwell hardness:  
ASTM D785—51 R scale

Tensile strength:

ASTM D638—61T

Unit: kg/cm<sup>2</sup>

- 30 Furthermore, in the following Examples, the content of vinyl monomeric unit graft/block copolymerized with mono-olefin polymer contained in the modified polymer composition is referred to as "graft/block amount", the content of vinyl monomeric unit forming a vinyl homopolymer which is not bound to the monoolefin polymer is referred to as "vinyl

homopolymer amount" and the percentage of "graft/block amount" to the total vinyl monomeric units contained in the modified polymer composition is referred to as "efficiency". 40

#### EXAMPLE 1:

With a powdered propylene polymer having an intrinsic viscosity of 4.8 as measured in tetralin at  $135^{\circ}\text{C}$ . and containing 98% of an insoluble portion in boiling n-heptane was mixed dicumyl peroxide. 45

The resulting mix was put into a hopper of a 60 mm. dia. screw extruder-type pelletizing machine provided with mixing torpedos and a sample feeding hole at center portion of the cylinder. On the other hand, there was supplied to the mix a predetermined amount of lauryl methacrylate through the sample feeding hole and the mix was melt kneaded and reacted at  $180^{\circ}\text{C}$ . under nitrogen atmosphere and extruded to give pellets of a modified polymer composition. 50 55

The composition of the modified polymer was varied by altering the amounts of dicumyl peroxide within the range of 0.3—1.0% and those of lauryl methacrylate within the range of 5—10%. 60

For comparison, there were prepared a sample from the modified polymer composition obtained above by removing homopolymer of lauryl methacrylate therefrom by extraction to give graft/block copolymer alone (cf. Experiment No. 2), and samples of blended polymers of propylene polymer and lauryl methacrylate homopolymer by simply blending these two ingredients (cf. Experiment No. 6 and 9). 65 70

The Drop-cone impact strength at  $-20^{\circ}\text{C}$ . and Rockwell hardness of these samples were measured with the results shown in Table 1. 75

TABLE 1

Experiment Nos.	Modified polymer composition			Mechanical properties		
	Copolymer-ized vinyl polymer (%)	Vinyl homo-polymer (%)	Ratio (%)	MI 230°C 2.16kg.	Drop-cone impact strength -20°C (kg-m)	Rockwell hardness (R scale)
1	0	0	—	4.8	0.12	84
2	4.9	0	100	4.4	0.58	81
3	2.5	2.3	52	4.1	4.2	81
4	1.2	3.7	24	4.6	3.6	78
5	0.4	4.4	8	4.0	1.6	69
6	0	5.0	0	5.2	1.3	67
7	4.9	4.4	53	4.3	8.6	72
8	2.3	6.9	25	5.4	5.7	70
9	0	10.0	0	5.2	2.1	64

5 In the above Table 1, Experiment Nos. 3, 4, 7 and 8 are compositions of this invention and Nos. 1, 2, 5, 6 and 9 are Comparative Examples.

10 It can be noted that in the modified polymer compositions of this invention, the low temperature impact strength is remarkably enhanced without being accompanied by any important deterioration in the hardness, thus, quite a well-balanced and practical modification of physical properties has been accomplished.

## EXAMPLE 2:

15 Modified polymer compositions were prepared according to the same procedures as described in Example 1 except that n-butyl methacrylate was substituted for lauryl methacrylate.

20 For comparison, a sample in which homopolymer was removed by extraction and a sample in which propylene polymer was blended with vinyl homopolymer were prepared.

25 The Izod impact strength and Rockwell hardness of these samples were measured with the results as shown in Table 2:

TABLE 2

Experiment Nos.	Modified polymer composition			Mechanical properties		
	Copolymer-ized vinyl polymer (%)	Vinyl homo-polymer (%)	Ratio (%)	MI 230°C 2.16kg.	Izod impact strength (notched) Ft-lb/in	Rockwell hardness (R scale)
1	0	0	—	4.8	0.28	84
2	4.7	0	100	5.2	0.32	82
3	2.6	2.0	56	5.0	0.92	81
4	1.8	2.9	38	4.4	0.97	80
5	0	5.0	0	4.3	0.42	72

8

In the above Table 2, Experiment Nos. 3 and 4 are compositions of this invention, while Nos. 1, 2 and 5 are Comparative Examples.

#### EXAMPLE 3:

- 5 Example 1 was repeated according to the same procedures as described therein except that an ethylene/propylene block copolymer having an intrinsic viscosity of 3.8, contain-

ing 96% of an insoluble portion in boiling n-heptane and having an ethylene content of 15 mol % was reacted with lauryl methacrylate in place of polypropylene.

The Drop-cone impact strength and the Rockwell hardness of the resulting modified polymer were measured with the results as shown in Table 3.

TABLE 3

Experiment Nos.	Modified polymer composition			Mechanical properties		
	Copolymerized vinyl polymer (%)	Vinyl homopolymer (%)	Ratio (%)	MI 230°C 2.16kg.	Drop-cone impact strength at -20°C (kg-m)	Rockwell hardness (R scale)
1	0	0	—	2.3	2.1	70
2	3.8	0	100	2.1	2.7	67
3	1.3	2.4	35	2.4	5.3	66
4	0	4.0	0	2.5	3.1	60

- 20 In the Table 3, the polymer composition of Experiment No. 2 was prepared by removing vinyl homopolymer by extraction from the modified polymer obtained by reacting ethylene/propylene block copolymer with lauryl methacrylate in the same manner.

- 25 The polymer composition of Experiment No. 4 was prepared by blending ethylene/propylene block copolymer mechanically with lauryl methacrylate homopolymer.

- 30 The Table 3 shows that in the polymer composition of Experiment No. 3 according to this invention, the Rockwell hardness is close to the original value of ethylene/propylene copolymer and the impact resistance is remarkably enhanced.

#### EXAMPLE 4:

- 35 A mixed polymer consisting of 60 parts by weight of powdered polypropylene having an intrinsic viscosity of 4.8 and 40 parts by weight of ethylene/propylene block copolymer having an intrinsic viscosity of 3.8 and an ethylene content of 15 mol % was reacted with 5% of lauryl methacrylate according to the same procedures as described in Example 1.

- 45 There was obtained a modified polymer having a Melt Index (230°C., 2.16kg) of 2.9, the total vinyl polymer content of 4.2% and the copolymerized vinyl polymer content of 1.4%.

- 50 The resulting modified polymer had a Rockwell hardness of 74, and a Drop-cone impact strength at -20°C. of 5.0, and the impact strength was remarkably improved with-

out being accompanied by deterioration in the hardness.

#### EXAMPLES 5—9:

55 With a powdered propylene having an intrinsic viscosity of 4.8 as measured in tetralin at 135°C. and containing 98% of an insoluble portion in boiling n-heptane were mixed predetermined amounts of dicumyl peroxide (hereinafter referred to as "DCP"). There is also employed cumyl hydroperoxide (hereinafter referred to as CHP). The resulting mix was put into a hopper of a 60 mm. dia. screw extruder-type pelletizing machine provided with mixing torpedos and a sample feeding hole at center portion of the cylinder, while there were fed predetermined amounts of n-butyl methacrylate into the mix through the sample feeding hole and the resulting mix was melt kneaded and reacted at 180°C. under nitrogen atmosphere and extruded to give pellets of a modified polymer.

60 The time required for the propylene polymer to pass the sample feeding hole after being fed into the hopper was about 2 minutes, and the time required for the mix to be extruded from the extruding hole into open air was about 5 minutes.

65 For comparison, the extrusions were repeated by mixing n-butyl methacrylate and the peroxide with propylene polymer simultaneously and putting the resulting mix into the hopper (hereinafter referred to as Comparative Example A), and by feeding propylene polymer from the hopper and feeding a mixture of n-butyl methacrylate and the peroxide



from the sample feeding hole provided at center portion of the cylinder (hereinafter referred to as Comparative Example B), while other conditions remained the same as described above.

- 5 The resulting modified polymer was dissolved in xylene and precipitated from acetone and the precipitates were subjected to the same dissolving and precipitating operations for several times. The resulting insoluble portion in acetone was extracted with acetone for 50 hours using a Soxhlet extractor to remove completely n-butyl methacrylate homopolymer

not bound to propylene polymer therefrom.

The modified polymer thus obtained was subjected to an infrared spectrography to determine the graft/block amount, i.e. the amount of n-butyl methacrylate unit bound to propylene polymer. On the other hand, the vinyl homopolymer amount was determined by subtracting the graft/block amount from the quantitative amount of n-butyl methacrylate unit contained in the modified polymer prior to the extraction operation. The results are shown in the following Table 4:

15  
20  
25

TABLE 4

	Nos.	Additives			Analysis		
		Type and amount of peroxide (%)	n-Butyl methacrylate (%)	Graft/block amount (%)	Vinyl homopolymer (%)	Efficiency (%)	
Comparative Example A	1	DCP 0.5	5.0	0.8	3.6	18	
	2	DCP 0.5	10.0	1.3	6.4	17	
	3	DCP 1.0	10.0	1.8	7.0	20	
	4	CHP 0.5	10.0	1.2	6.3	16	
	5	CHP 1.0	10.0	1.6	7.1	18	
Comparative Example B	1	DCP 0.5	10.0	1.5	7.2	17	
	2	DCP 1.0	10.0	1.8	7.4	20	
	3	CHP 0.5	10.0	1.5	7.0	18	
Examples	5	DCP 0.5	5.0	2.5	2.1	54	
	6	DCP 0.5	10.0	2.7	6.5	29	
	7	DCP 1.0	10.0	4.7	4.3	52	
	8	CHP 0.5	10.0	1.9	7.1	21	
	9	CHP 1.0	10.0	3.1	6.1	34	

- 30 As can be noted from the Comparative Examples A and B, when n-butyl methacrylate is reacted with propylene polymer in the presence of peroxide, there was observed practically no change in the ratio of graft/block amount to vinyl homopolymer amount and the efficiency was within the range of 16—20%, even if the reactions were conducted by changing the amounts of respective additives or the type of peroxide.

35 In contrast, it is understood from the Examples 5—9 according to this invention that the modified polymers obtained therein show

a wider range of efficiency variation, e.g. 21—54%, and further that the values of efficiency are high. It is clear that such a unique effect is only attainable according to this invention.

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#### EXAMPLES 10—12:

45 With the same powdered propylene polymer as used in Examples 5—9 was mixed 0.5% of dicumyl peroxide (DCP) and the resulting mixture was put into the hopper of the same screw extruder-type pelletizing machine as used in Examples 5—9. On the other hand, 50 lauryl methacrylate was fed into the mix

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through the sample feeding hole provided at center portion of the cylinder so that the amount may be 10% based on propylene polymer and the mix was melt kneaded and reacted at 180°C. under nitrogen atmosphere and continuously extruded to give pellets of a modified polymer.

In the operation described above, the time required for the mixture of propylene polymer and peroxide to contact with vinyl monomer after starting of the heating, i.e. the time required for the mixture to pass through the sample feeding hole on the cylinder after

being put into the hopper, was varied for 1, 2 and 4 minutes.

The results of analysis of the modified polymer thus obtained are shown in Table 5.

For comparison, the above-mentioned Examples were repeated according to the same procedures as described therein except that propylene polymer, DCP and lauryl methacrylate were put into the hopper simultaneously and nothing was fed from the sample feeding hole, as Comparative Example C.

TABLE 5

	Nos.	Extrusion rate (min)	MI 230°C 2.16kg	Analysis		
				Graft/block amount (%)	Vinyl homopolymer amount (%)	Efficiency (%)
Comparative	1	1	1.7	1.8	7.7	19
Example	2	2	1.9	1.7	7.6	17
C	3	4	2.3	1.9	7.6	20
Examples	10	1	2.1	2.9	6.7	30
	11	2	3.5	3.4	6.3	38
	12	4	4.6	1.8	7.4	20

In the modified polymers obtained in Comparative Examples C1—C3, although the reaction time in the extruder was varied in a wide range, practically no variation in the efficiency was observed and it remained with the range of 17—20%.

In contrast, the modified polymers obtained in the Examples 10—12 according to this invention in which the degree of decomposition of DCP contained therein was changed by varying the time required for the mixture of propylene polymer and DCP to contact with vinyl monomer after starting of the heating show a wide variation in the ratio of graft/block copolymerized vinyl monomer to vinyl homopolymer, e.g. in the range of 20—38%.

#### EXAMPLES 13 and 14:

With a powdered propylene polymer having an intrinsic viscosity of 13.4 as measured in tetralin at 135°C. and containing 98% of an insoluble portion in boiling n-heptane was

mixed 0.3% of  $\alpha,\alpha'$ -bis(t-butyl peroxy)-p-diisopropylbenzene.

The resulting mix was put into the hopper of the same screw extruder-type pelletizing machine as used in Examples 5—9, while acrylic acid was fed into the mix through the sample feeding hole provided on the cylinder so that the amount was 5% based on propylene polymer and the mix was melt kneaded and reacted at 180°C. or 230°C. under nitrogen atmosphere and continuously extruded to give pellets of modified polymers. The time required for the mixture to contact with acrylic acid after being put into the hopper was 2 minutes.

The results of analysis of the modified polymers thus obtained are shown in Table 6. In the Comparative Example D referred to therein, propylene polymer, peroxide and vinyl monomer were put into the hopper of the screw extruder-type pelletizing machine simultaneously.

TABLE 6

	Nos.	Reaction temperature (°C)	MI 230°C 2.16kg	Analysis		
				Graft/block amount (%)	Vinyl homopolymer amount (%)	Efficiency (%)
Comparative Example D	1	180	7.2	1.0	3.4	22
	2	230	8.1	1.1	3.2	25
Examples	13	180	8.2	2.3	2.1	51
	14	230	9.6	1.6	2.9	36

It is understood from the results shown above that the amounts of acrylic acid graft/block copolymerized with propylene polymer are high in the modified polymers obtained according to this invention, e.g. 36—51%, and greatly affected by the reaction temperature, in contrast with the cases of Comparative Examples in which peroxide and acrylic acid are reacted simultaneously with the results showing that the amounts are rather insensitive to the variation in the reaction temperature, e.g. remaining within the range of 22—25%.

Thus, it is clear that the process of this invention enables the production of modified polymer compositions most suitable for the use contemplated.

#### WHAT WE CLAIM IS:—

1. A process for the production of a modified mono-olefin polymer composition which comprises treating a mono-olefin polymer (as herein defined) with a radical-generating initiator and reacting the product with a vinyl monomer (as herein defined) in the molten state and with agitation of the reaction mixture, whereby part of the vinyl monomer is graft or block copolymerised with the mono-olefin polymer and part is polymerised *per se*, the total of the vinyl monomer thus copolymerised or polymerised constituting 3 to 30% by weight based on the weight of the mono-olefin polymer and the proportion of the said total of vinyl monomer so polymerised or copolymerised which is graft or block copolymerised with the mono-olefin polymer being 10 to 65% by weight of such total.

2. A process according to claim 1 wherein the mono-olefin polymer is a homopolymer of an olefin selected from ethylene, propylene, butene-1, 3-methyl butene-1, 4-methyl-pentene-1 and styrene or a copolymer selected

from ethylene/propylene copolymer, ethylene/propylene block copolymer, ethylene/butene copolymer, ethylene/vinyl acetate copolymer, ethylene/ethyl acrylate copolymer, and propylene/4-methylpentene-1 copolymer, or mixtures thereof.

3. A process according to claim 1 or 2 wherein the vinyl monomer is selected from styrene and derivatives thereof, acrylic acid, methacrylic acid, esters, amides and metal salts of acrylic acid and methacrylic acid, vinyl esters, allyl esters, and polycyclic and heterocyclic vinyl compounds, other monoethylenically unsaturated monomers, and monomers having two or more vinyl groups.

4. A process according to any of claims 1—3 wherein the radical generating initiator is dicumyl peroxide.

5. A process according to any of claims 1—3 wherein the radical-generating initiator is  $\alpha, \alpha'$ -bis (*t*-butyl peroxy)-*p*-di-isopropyl benzene.

6. A process according to any of claims 1—3 wherein the radical generating initiator is di-*t*-butyl peroxide.

7. A process according to any of the preceding claims wherein the reaction temperature is from 0° to 100°C. above the melting point of the mono-olefin polymer used.

8. A process according to claim 1 substantially as hereinbefore described with reference to any one of the foregoing specific Examples 1—14.

9. A modified mono-olefin polymer composition prepared by the process of any of claims 1—8.

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